

# Experimental evidence for Shekhtman-Entin-Wohlman-Aharony (SEA) interactions in $\text{Ba}_2\text{CuGe}_2\text{O}_7$

A. Zheludev<sup>(1)</sup>, S. Maslov<sup>(1)</sup>, I. Tsukada<sup>(2)</sup>, I. Zaliznyak<sup>(3,4)</sup>, L. P. Regnault<sup>(5)</sup>, T. Masuda<sup>(2)</sup>, K. Uchinokura<sup>(2)</sup>, R. Erwin<sup>(3)</sup>, G. Shirane<sup>(1)</sup>

(1) Brookhaven National Laboratory, Upton, NY 11973-5000, USA. (2) Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. (3) NIST Center for Neutron Research, National Institute of Standards and Technology, MD 20899, USA. (4) Department of Physics and Astronomy, Johns Hopkins University, MD 21218 USA, and P. L. Kapitza Institute for Physical Problems, Moscow, Russia. (5) RFMC/SPSMS/MDN, CENG, 17 rue des Martyrs, 38054 Grenoble Cedex, France.

(February 1, 2008)

New neutron diffraction and inelastic neutron scattering experiments on  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  suggest that the previously suggested model for the magnetism of this material (an ideal sinusoidal spin spiral, stabilized by isotropic exchange and Dzyaloshinskii-Moriya interactions) needs to be refined. Both new and previously published experimental results can be quantitatively explained by taking into account the Shekhtman-Entin-Wohlman-Aharony (SEA) term, a special anisotropy term that was predicted to always accompany Dzyaloshinskii-Moriya interactions in insulators. Our experimental results present the first clear evidence to that SEA interactions can lead to substantial observable effects in a real magnetic system.

75.30.Et, 75.10.Hk, 75.30.Ds, 75.30.Gw

Among the more exotic magnetic interactions in solids is the so-called asymmetric exchange, first predicted theoretically by Dzyaloshinskii [1]. Unlike conventional Heisenberg exchange coupling, that is proportional to the *scalar* product  $\mathbf{S}_1 \cdot \mathbf{S}_2$  of interacting spins, asymmetric exchange is proportional to the corresponding *vector* product. In the spin Hamiltonian it is usually written as  $\mathbf{D}(\mathbf{S}_1 \times \mathbf{S}_2)$ , where  $\mathbf{D}$  is the Dzyaloshinskii vector associated with the bond between the two interacting magnetic ions. A microscopic model for asymmetric exchange interactions was first proposed by Moriya [2], and is essentially an extension of the Anderson superexchange mechanism [3], that allows for spin-flip hopping of electrons. While forbidden by symmetry in centrosymmetric crystal structures, Dzyaloshinskii-Moriya (DM) interactions were found to be active in a number of non-centric compounds, where they lead to either a weak ferromagnetic- or helimagnetic- distortion of the collinear magnetic state [4,5,6]. The inclusion of the DM term breaks  $O(3)$  invariance of the originally isotropic Heisenberg spin Hamiltonian, reducing the symmetry to  $O(2)$ : to take full advantage of the cross product term the interacting spins must be perpendicular to the vector  $\mathbf{D}$ . DM interactions thus play a role of an effective two-ion easy-plane anisotropy, with the easy plane normal to the vector  $\mathbf{D}$ .

Only recently Shekhtman, Entin-Wohlman and Aharony realized that there is *more* to Moriya's mech-

anism than just the vector-product term [7,8]. For very fundamental reasons the DM cross-product must always be accompanied by a two-ion easy axis anisotropy term that exactly compensates the easy-plane effect of the vector product. The additional (SEA) term can to a good approximation be written as  $\frac{1}{2J}(\mathbf{S}_1 \mathbf{D})(\mathbf{S}_2 \mathbf{D})$ , where  $J$  is the Heisenberg (isotropic) component of superexchange coupling. Often referred to as “hidden symmetry”, the SEA term *restores*  $O(3)$  invariance of the Hamiltonian, at least locally. Originally, the SEA term was invoked to explain the spin anisotropy in the orthorhombic phase of  $\text{La}_2\text{CuO}_4$  [7,8,9]. It was later realized that this term alone can not account for all the observed effects, particularly for the magnetic anisotropy seen in the tetragonal phase [10,11,12]. To our knowledge, to date there has been no “clean” experimental evidence unambiguously pointing to the presence of SEA interactions. In the present paper we present such experimental data for the helimagnetic insulator  $\text{Ba}_2\text{CuGe}_2\text{O}_7$ . We demonstrate that only by taking into account the SEA term one can obtain qualitatively and quantitatively correct predictions for the magnetic structure and spin wave spectrum.

As was shown in a series of recent publications [13,14,15,16],  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  is a particularly useful model system for studying DM interactions. The magnetism of this compound is due to  $\text{Cu}^{2+}$  ions that form a square lattice in the  $(a, b)$  tetragonal plane of the crystal. The principal axes of this square lattice, hereafter referred to as the  $x$  and  $y$  axis, run along the  $[110]$  and  $[1\bar{1}0]$  crystallographic directions, respectively. To complete the coordinate system we shall choose the  $z$  along the  $[001]$  direction. In the magnetically ordered phase (below  $T_N = 3.2$  K) all spins lie in the  $(1\bar{1}0)$  plane. The magnetic propagation vector is  $(1 + \zeta, \zeta, 0)$ , where  $\zeta = 0.0273$ , and  $(1, 0, 0)$  is the antiferromagnetic zone-center. The magnetic structure is a distortion of a Néel spin arrangement: a translation along  $(\frac{1}{2}, \frac{1}{2}, 0)$  induces a spin rotation by an angle  $\phi = 2\pi\zeta \approx 9.8^\circ$  (relative to an exact antiparallel alignment) in the  $(1, -1, 0)$  plane. Along the  $[1\bar{1}0]$  direction nearest-neighbor spins are perfectly antiparallel. Spins in adjacent Cu-planes are aligned parallel to each other. Only nearest-neighbor in-plane isotropic

superexchange antiferromagnetic interactions are important ( $J \approx 0.96$  meV, as determined by the measured spin wave bandwidth [13]). The helical state is stabilized by DM interactions. In the current model Dzyaloshinskii vectors for nearest-neighbor Cu-Cu pairs lie in the  $(x, y)$  plane and are oriented perpendicular to their corresponding bonds:  $\mathbf{D} \parallel y$  for an  $x$ -bond and  $\mathbf{D} \parallel x$  for  $y$ -bonds, respectively (Fig. 1 in Ref. [15]). The corresponding energy scale is  $D \approx 0.17$  meV. In the discussion below we shall use the numerical values for  $J$  and  $\zeta$  quoted above as given, and perform all calculations without using any adjustable parameters.

The magnetic structure of  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  is expected to be particularly sensitive to the presence of SEA interactions. Indeed, in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  SEA easy axes that correspond to the  $y$ -Cu-Cu bonds are parallel to the  $x$  axis, i.e., are *in the plane of spin rotation*. Regions of the slowly rotating spin spiral where the local staggered magnetization  $\mathbf{l}$  is almost parallel to  $x$  become more energetically favorable than those where  $\mathbf{l}$  is almost parallel to  $z$  (crystallographic  $c$ -axis). SEA anisotropy must therefore lead to a distortion of the ideal sinusoidal spiral, and modify the period of the structure. The SEA term is expected to produce exactly the same distortion as a magnetic field  $H$  applied along the  $z$  axis: the latter also has the effect of forcing the local staggered magnetization into the  $(x, y)$  plane. The role of a  $z$ -axis field is rather dramatic and has been studied in detail [15,16]. The period of the spiral increases with increasing  $H$  and diverges at  $H_c \approx 2.15$  T, resulting in a commensurate spin-flop antiferromagnetic state at  $H > H_c$ . For  $0 < H < H_c$  the spin structure is described as a “soliton lattice” where regions of the commensurate phase are interrupted by regularly spaced antiferromagnetic domain walls. In the soliton phase, in addition to the principal magnetic Bragg peaks at  $(1 \pm \zeta, \pm \zeta, 0)$ , characteristic of an ideal spiral, one expects to see all odd magnetic Bragg harmonics at  $(1 \pm 3\zeta, \pm 3\zeta, 0)$ ,  $(1 \pm 5\zeta, \pm 5\zeta, 0)$ , etc. By comparing the experimental field dependencies of  $\zeta$  and the higher-order Bragg peaks to theoretical predictions for the “DM-only” (Ref. [15,16]) and “DM+SEA” models we can hope to obtain direct evidence for SEA interactions in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$ .

We can make the above discussion quantitative by including the SEA term into the phenomenological energy functional that was previously used to describe the behaviour of  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  in the framework of the DM-only model [15,16]. This procedure is rather straightforward and the principal conclusion is that all previously obtained DM-only results can be recycled, by replacing  $H$  in all equations by the *effective* field

$$H^{\text{eff}} = \sqrt{H^2 + 2A\rho_S/(\chi_\perp - \chi_\parallel)}. \quad (1)$$

Here  $\rho_S \approx JS^2$  is the spin stiffness,  $\chi_\perp$  and  $\chi_\parallel$  are the local transverse and longitudinal susceptibilities, respec-

tively, and the SEA term is represented by  $A = \alpha^2/2 \approx D^2/2J^2$ . The parameter  $\alpha$  is defined by  $\tan \alpha \equiv D/J$ , and is equal to the spin rotation angle  $\phi$  in the DM-only model. According to our continuous-limit calculations, in the DM+SEA model  $\alpha \equiv \arctan(D/J) = \frac{32}{31}\phi$ .

First, let us consider the field dependence of the incommensurability parameter  $\zeta$  that for the DM+SEA model can be obtained by replacing  $H$  by  $H^{\text{eff}}$  in Eqs. 4 and 7 in Ref. [15]:

$$\frac{\zeta(H)}{\zeta(0)} = \frac{\pi^2}{4E(\beta)K(\beta)} \quad (2)$$

$$\frac{H^{\text{eff}}}{H_c^{\text{eff}}} = \frac{\beta}{E(\beta)} \quad (3)$$

Here  $\beta$  is an implicit variable and  $K$  and  $E$  are complete elliptic integrals of the first and second kind, respectively. In Fig. 1 we replot the  $\zeta(H)$  data from Ref. [15] in reduced coordinates. The solid and dashed lines are the theoretical curves plotted with and without taking into account SEA interactions, respectively. We see that the inclusion of the SEA term hardly affects the *shape* of the  $\zeta(H)$  curve. However, the theoretical prediction for  $H_c$  is substantially different in the DM-only and DM+SEA models. Combining Eq. 1 from above with Eq 5 in Ref. [15] one readily obtains:

$$H_c = \alpha \frac{\sqrt{\pi^2 - 4}}{2} \sqrt{\frac{\rho_s}{\chi_\perp - \chi_\parallel}}, \quad (4)$$

For the low-temperature limit in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  we can use the classical expressions  $\rho_s = JS^2 = 0.24$  meV,  $\chi_\parallel = 0$  and  $\chi_\perp = (g_c\mu_B)^2/8J$ , where  $g_c = 2.47$  is the  $c$ -axis gyromagnetic ratio for  $\text{Cu}^{2+}$  in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  [17]. One can expect these classical estimates to be rather accurate, as they rely on the *effective* exchange constant  $J$ , that itself was determined from fitting the *classical* spin wave dispersion relations to inelastic neutron scattering data [13]. Substituting  $\alpha = 2\pi\frac{32}{31}\zeta = 0.177$ , we get the estimate for the critical field  $H_c = 2.05$  T. This value is much closer to the experimental value  $H_c \approx 2.15$  T, than our previous estimate  $H_c \approx 2.6$  T [18], obtained without taking into account the SEA term.

As mentioned, SEA interactions have a substantial influence on the intensity of higher-order Bragg harmonics. In the DM-only model in zero field higher-order Bragg reflections are totally absent. For the DM+SEA model, combining our expression for  $H^{\text{eff}}$  with Eqs. 17,18 in Ref. [16], for the relative intensities of the 1st and 3rd harmonics, in the small field limit (weakly distorted spiral)  $|\phi - \alpha| \ll \phi$  we get:

$$\frac{I_3}{I_1} = \left[ \frac{1}{16} + \left( \frac{\pi^2}{64} - \frac{1}{16} \right) \left( \frac{H}{H_c} \right)^2 \right]^2 \quad (5)$$

In zero field this gives  $I_3/I_1 = 1/256 \approx 4 \times 10^{-3}$ . To verify the relation (5) we performed new magnetic neu-

tron scattering experiments on  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  single crystal samples. The measurements were done in two experimental runs, on the IN-14 3-axis spectrometer at the Institut Laue Langevin (ILL) in Grenoble, and the SPINS spectrometer at the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST). The samples were similar to those used in previous studies [16]. In each experiment the crystals were mounted with their  $c$ -axes vertical, making  $(h, k, 0)$  wave vectors accessible for measurements. The magnetic field was produced by standard split-coil superconducting magnets. The sample environment was either a pumped- $^4\text{He}$  or pumped- $^3\text{He}$  cryostat. The data were collected at temperatures in the range 0.35–5 K. Neutrons of energies 3.5 meV or 2.5 meV were used in most cases. A  $40' - S - 40' - A - 40'$  collimation setup was used with a Be filter positioned in front of the sample. In Fig. 2(a,b) we show some typical elastic scans along the  $(1 + \epsilon, \epsilon, 0)$  reciprocal-space line measured in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  at low temperatures in zero and  $H = 1$  T applied fields. Even in the zero-field data in addition to the 1st-order principal magnetic reflection one clearly sees the 3rd order harmonic. The measured field dependence of  $I_3/I_1$  (ratio of  $Q$ -integrated intensities) is shown in Fig. 2(c). In our measurements we have taken special care to verify that the relative intensities of the two peaks are totally independent of the  $T-H$  history of the sample. The solid and dashed lines in Fig. 2(c) represent the predictions of the DM+SEA (Eq. 5) and DM-only (Ref. [15,16]) models, respectively. For these theoretical curves we used the same numerical values as in our estimates for  $H_c$ , and no adjustable parameters. An almost perfect agreement between the DM+SEA model and the experimental data is apparent, and so is the failure of the DM-only model.

It is clear that the SEA anisotropy term, in addition to modifying the ground state, will affect the spin wave spectrum. For an ideal spin spiral (DM-only model) the classical spin wave dispersion relations can easily be obtained analytically using the Holstein-Primakov formalism. The result of such a calculation for  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  is shown in Fig. 3(a). Two acoustic branches (hereafter referred to as the  $\pm\zeta$  modes) emerge from the two magnetic Bragg peaks at  $(1 \pm \zeta, \zeta, 0)$ . A third branch (the 0-mode) has a gap at the antiferromagnetic zone-center, equal to the Dzyaloshinskii parameter  $D$ . This branch almost exactly passes through the intersection point of the  $\pm\zeta$  modes. The actual dispersion curves in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  were measured in constant- $Q$  inelastic scans using the experimental setups described above in the fixed-incident-energy mode. In these experiments the typical energy resolution, as measured by scanning through incoherent scattering, was 0.075 meV FWHM at zero energy transfer. A strong incoherent signal and the “tails” of magnetic Bragg reflections prevented us from collecting reliable data for energy transfers of less than  $\approx 0.17$  meV. A typical inelastic scan (raw data) is shown in Fig. 4.

Combined data from the two series of experiments are summarized in the experimental dispersion relations in Fig. 3(b) (symbols). Two prominent features of the measured dispersion curves are to be discussed here. i) The two  $\pm\zeta$  modes do not intersect at the Néel point. Instead, at  $Q = (1, 0, 0)$  there is a clear repulsion between these two branches. This repulsion is again manifest at  $Q = (1 + 2\zeta, 2\zeta, 0)$  and is seen as a discontinuity in the  $+\zeta$ -branch. ii) At the antiferromagnetic zone-center the 0-mode lies visibly lower than the extrapolated point of intersection of the  $\pm\zeta$  branches (dashed lines). Obviously, the DM-only model fails to reproduce the observed dispersion relations. An exact analytical calculation of the spin wave spectrum in the presence of SEA interactions is not possible. However, in the limit  $|\phi - \alpha| \ll \phi$ , a condition well satisfied in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  in zero applied field, one can use the series expansion method described in Refs. [19,20], and leaving only the lowest-order terms in  $A$ . Performing this somewhat tedious calculation for  $\text{Ba}_2\text{CuGe}_2\text{O}_7$ , we obtain the dispersion relations shown in solid lines in Fig. 3(b), and find very good agreement with experiment with *no adjustable parameters*.

In summary, both the static and dynamic magnetic properties of  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  contain *quantitative* evidence of the SEA anisotropy term. The issue that we tried to address above is not whether or not SEA interactions *exist*: if one believe Anderson’s and Moriya’s superexchange mechanisms, one is forced to accept the presence of the SEA term as well. Rather, our results for the first time show that SEA interactions can result in very interesting measurable effects in a real magnetic system. We also would like to emphasize that the new results do not undermine our previous conclusions regarding the commensurate-incommensurate Dzyaloshinskii transition in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$ . The transition occurs exactly as described, only now we have a more accurate theoretical estimate for the critical field  $H_c$ .

This study was supported in part by NEDO (New Energy and Industrial Technology Development Organization) International Joint Research Grant and the U.S. -Japan Cooperative Program on Neutron Scattering. Work at BNL was carried out under Contract No. DE-AC02-76CH00016, Division of Material Science, U.S. Department of Energy. Experiments at NIST were partially supported by the NSF under contract No. DMR-9413101.

- 
- [1] I. Dzyaloshinskii, Soviet Physics-JETP **5**, 1259 (1957).
  - [2] T. Moriya, Phys. Rev. **120**, 91 (1960).
  - [3] P. W. Anderson, Phys. Rev. **115**, 2 (1959).
  - [4] Y. Ishikawa, G. Shirane, J. Tarvin, and M. Kohgi, 1977.

- [5] Y. Ishikawa and M. Arai, J. Phys. Soc. Japan **53**, 2726 (1984).
- [6] B. Lebech, J. Bernhard, and T. Flertoft, J. Phys: Condens. Matter **1**, 6105 (1989).
- [7] L. Shekhtman, O. Entin-Wohlman, and A. Aharony, Phys. Rev. Letters **69**, 836 (1992).
- [8] L. Shekhtman, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B **47**, 174 (1993).
- [9] O. Entin-Wohlman, A. Aharony, and L. Shekhtman, Phys. Rev. B **50**, 3068 (1994).
- [10] W. Koshibae, Y. Ohta, and S. Maekawa, Phys. Rev. Letters **71**, 467 (1993).
- [11] T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. Letters **73**, 2919 (1994).
- [12] T. Yildirim, A. B. Harris, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B **52**, 10239 (1995).
- [13] A. Zheludev *et al.*, Phys. Rev. B **54**, 15163 (1996); Physica B **234-236**, 546 (1997).
- [14] A. Zheludev *et al.*, Phys. Rev. B **56**, 14006 (1997).
- [15] A. Zheludev *et al.*, Phys. Rev. Letters **78**, 4857 (1997).
- [16] A. Zheludev *et al.*, Phys. Rev. B **57**, 2968 (1998).
- [17] Y. Sasago, unpublished ESRdata.
- [18] The numerical estimate for the critical field in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  (DM-only model), quoted in Refs. [15,16] ( $H_c = 3.3$  T) is incorrect. Substituting the classical parameters listed in the end of Ref. [15] into the expression for  $H_c$  in the same paper, one actually gets  $H_c = 2.6$  T.
- [19] M. E. Zhitomirsky and I. A. Zaliznyak, Phys. Rev. B **53**, 3428 (1996).
- [20] I. A. Zaliznyak and M. E. Zhitomirsky, Zh. Exp. Teor. Fiz. **108**, 1052 (1995) [JETP **81**, 579 (1995)].

FIG. 1. Field dependence of the incommensurability parameter  $\zeta$ , as previously measured in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  (Refs. [15,16]). The solid and dashed lines are theoretical predictions that do (this work) or do not (Ref. [15]) take into account SEA interactions, respectively.

FIG. 2. Typical elastic scans along the  $(1,1,0)$  direction in the vicinity of the antiferromagnetic zone-center  $(1,0,0)$ , measured in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  at  $T = 0.35$  K in zero field (a) and in a  $H = 1.6$  T magnetic field applied along the  $c$ -axis (b). (c) The square root of the measured ratio of the intensities of the  $(1 + 3\zeta, 3\zeta, 0)$  and  $(1 + \zeta, \zeta, 0)$  peaks plotted against the square of the applied field. The lines are guides for the eye in (a) and (b) and theoretical curves in (c), as in Fig. 1.

FIG. 3. (a) Classical spin wave dispersion relations calculated for  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  without taking into account SEA interactions. (b) Solid lines: same, with the SEA term included. Symbols: experimental dispersion curves measure in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  at  $T = 0.35$  K and  $T = 1.5$  K with inelastic neutron scattering.

FIG. 4. Typical inelastic scans measured in  $\text{Ba}_2\text{CuGe}_2\text{O}_7$  at  $T = 1.5$  K and  $T = 3$  K (combined data in lower plot). The shaded curves represent the individual Gaussians in a multi-peak fit (heavy solid line). The gray area shows the position of a “Bragg-tail” spurious peak.







